

9-22-2021

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A. A. Nogai

*L.N. Gumilyov Eurasian National University, Kazakhstan*

Zh. M. Salikhodzha

*L.N. Gumilyov Eurasian National University, Kazakhstan*

A. S. Nogai

*S.Seifulin Kazakh AgroTechnical University, Kazakhstan*

D. E. Uskenbaev

*S.Seifulin Kazakh AgroTechnical University, Kazakhstan,*

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### Recommended Citation

Nogai, A. A.; Salikhodzha, Zh. M.; Nogai, A. S.; and Uskenbaev, D. E. (2021) "Conducting and dielectric properties of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$ ," *Eurasian Journal of Physics and Functional Materials*: Vol. 5: No. 3, Article 7.

DOI: <https://doi.org/10.32523/ejpfm.2021050307>

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# Conducting and dielectric properties of $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ and $\text{Na}_2\text{FePO}_4\text{F}$

A.A. Nogai<sup>\*,1</sup>, Zh.M. Salikhodzha<sup>1</sup>, A.S. Nogai<sup>2</sup>,  
D.E. Uskenbaev<sup>2</sup>

<sup>1</sup>L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan

<sup>2</sup>S. Seifulin Kazakh Agro Technical University, Nur-Sultan, Kazakhstan

E-mail: nogay0.6@mail.ru

DOI: 10.32523/ejpfm.2021050307

Received: 17.08.2021 - after revision

In this research, the structure parameters, conducting and dielectric properties of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals were studied obtained by solid-phase synthesis. The phase transition temperatures, conducting and dielectric parameters of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals were refined. A comparative evaluation of the conductive properties of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals is given in this article. The prospects of using of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  are justified as electrode materials in sodium ion batteries.

**Keywords:** solid state synthesis, polycrystal, crystal framework, ionic conductivity, dielectric permittivity.

## Introduction

Nowadays, the demand for lithium-ion batteries (LIB) is increasing, but due to the limited lithium reserves on Earth, it is necessary to develop alternative options for metal-ion batteries. Such an alternative can be the development of efficient sodium-ion batteries (SIB) [1], since sodium is more common in nature and its cost is much lower than lithium, and the SIB itself is safer to operate than LIB. Promising SIB can have a high specific energy consumption, resistance to multiple cycling, a fast charge/discharge process, and the absence of a "memory effect" [2, 3].

At present, it is established that  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is a promising electrode material for SIB [4-7]. The basis of the crystal structure of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is the rhombohedral crystal framework  $\{[\text{Fe}_2(\text{PO}_4)_3]^{3-}\}_{3\infty}$ , which belongs to the NASICON structural type [8]. The anionic crystal framework of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is formed from  $\text{FeO}_6$  octahedra and  $\text{PO}_4$  tetrahedra, forming extensive voids of types A and B types and three-dimensional conduction channels [9, 10]. Moreover, in  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  sodium cations are placed only in large voids of B type (A cavities are empty), and in  $\gamma$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  the distribution of cations is uniform across all A and B types of voids. It is established that when  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is heated, successive phase transitions  $\alpha \rightarrow \beta$  occur from the monoclinic  $\alpha$ -phase ( $C2/m$ ) to the rhombohedral ( $3\bar{R}c$ )  $\beta$ -phase, which has superstructural reflexes. Superstructural reflexes disappear during the phase transition of  $\beta \rightarrow \gamma$  to the rhombohedral  $\gamma$ -phase [8, 9, 11]. For  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is characterized by the presence of a superstructural unit cell with an antiferroelectric type of dipole ordering, although in the  $\gamma$ -phase  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is in the superionic condition [11].

Nowadays, it is known that a porous cathode material based on  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , has a sufficiently high specific energy capacity of  $92.5 \text{ mAh/g}^{-1}$  in SIB [12]. It is noted in research works [12, 13] that  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  can be used as a promising anode material for aqueous SIB.  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is also a promising structural material for SIB.

The cathode based  $\text{Na}_2\text{FePO}_4\text{F}$  can provide up to  $110 \text{ mAh/g}^{-1}$ , energy consumption in the SIB, as well as stable cycling and low volume change during intercalation and deintercalation processes [14, 15]. It was considered that the crystal framework of  $\beta$ - $\text{Na}_2\text{FePO}_4\text{F}$  at room temperature has an orthorhombic syngony (e.g.,  $Pbcn$ ) and a layered structure [5-16]. The crystal framework  $\text{Na}_2\text{FePO}_4\text{F}$  is characterized by the presence of two-dimensional layers of chains connected along the vertices of the  $\text{Fe}_2\text{O}_6\text{F}_3$  bioctahedra along the crystal direction  $a$  [100], connected by  $\text{PO}_4$  tetrahedra in the crystal direction  $c$  [001]. Although sodium cations can diffuse in the space between the layers of the crystal framework, interlayer diffusion is practically impossible [16].

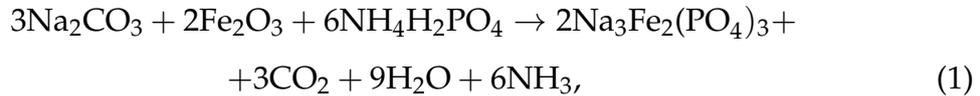
It was considered that the crystal structure of  $\alpha$ - $\text{Na}_2\text{FePO}_4\text{F}$  is characterized by a long-range antiferromagnetic order below 3.4 K, in which the ferromagnetic ordering of chains through phosphate groups along the  $c$  axis is possible, and the ordering can also be along the  $b$  axis [17]. This ordering is probably related to the contribution of the dipole-dipole interaction to  $\alpha$ - $\text{Na}_2\text{FePO}_4\text{F}$ .

Due to the discovery of electrochemical properties that are valuable from a practical point of view in these sodium - iron ortho- and fluoride phosphates, a more detailed study of the conducting and dielectric properties of these materials is of interest.

This research purpose of is to synthesize samples, study the structure, conducting and dielectric properties of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  and a comparative analysis of the results obtained, as well as the establishment of distinctive features of the conducting properties of these samples.

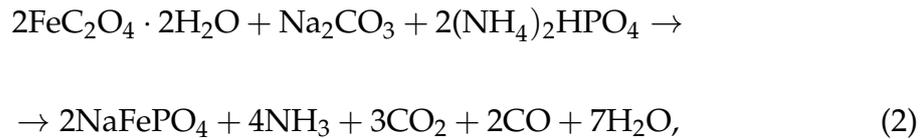
## Experimental part

Polycrystals  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  were obtained by solid-phase synthesis. For the synthesis of samples, we used highly pure salts and oxides:  $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{Fe}_2\text{O}_3$ . Solid-phase synthesis was carried out in two stages, in accordance with the reaction:



At the first stage, the annealing was carried out at 870 K, at the second stage, the temperature was 970 K, and the additional homogenizing grindings were added. The duration of the process of each stage of solid-phase synthesis of samples was 8 hours.

The preparation of polycrystals  $\text{Na}_2\text{FePO}_4\text{F}$  was carried out by solid-phase synthesis using preliminary mechanical activation of a mixture of reagents taken in stoichiometric ratios. The synthesis was carried out in two stages, in accordance with the reaction:



At the first stage, the annealing was carried out at 620 K, and the second stage, the temperature was 880 K in an argon atmosphere with additional homogenizing grinding were added. The duration of the process of each stage of solid-phase synthesis of samples was 8 hours.

The phase state and the structural parameters of polycrystalline samples of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  were examined by the X-ray diffraction powder method using the DRON-3 diffractometer ( $\text{CuK}_\alpha$  radiation).

The determination of the conducting and dielectric properties of the synthesized samples was carried out by the method of impedance spectroscopy using the VM-507 and VM-538 impedance meters in the temperature range of 295-573 K, in the frequency range  $5 \cdot 10^5$  and  $5 \cdot 10^5 - 10^8$  Hz respectively [11].

Based on the experimental data of the polycrystal impedance, the specific conductivity of the crystallites ( $\sigma_{cr}$ ) of polycrystalline samples were calculated according to the formula [11]:

$$\sigma_{cr} = \frac{d}{S} \frac{1}{\bar{Z}'_{cr}}, \quad (4)$$

where  $d$ -and  $S$ -thickness and area of the polycrystalline sample,  $\bar{Z}'_{cr}$  real components of the impedance of a polycrystal crystallite.

The dielectric permittivity of the crystallites ( $\varepsilon_{cr}$ ) of polycrystalline samples was calculated by the formula:

$$\varepsilon_{cr}^1 = \frac{d}{S} \frac{1}{\vec{Z}_{cr}''(\omega)}, \quad (5)$$

where  $j \vec{Z}_{cr}''(\omega)$ -imaginary components of the impedance of a polycrystal crystallite.

## Results and discussion

*Results of synthesis and X-ray research of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals.*

Synthesized polycrystals of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  had dark pink and pale pink colors, respectively. Both samples were tablets with a diameter of 10 mm and a thickness of 1 mm. The single-phase nature of the prepared samples was established by X-ray measurements. Figure 1 shows the diffractograms of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$   $\text{Na}_2\text{FePO}_4\text{F}$  powders at room temperature ( $T=295\text{K}$ ).  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  unit cell at room temperature has a rhombic syngony with a monoclinic distortion (e.g. gr.  $C2/m$ ), and the established structural parameters of the sample are presented in Table 1.

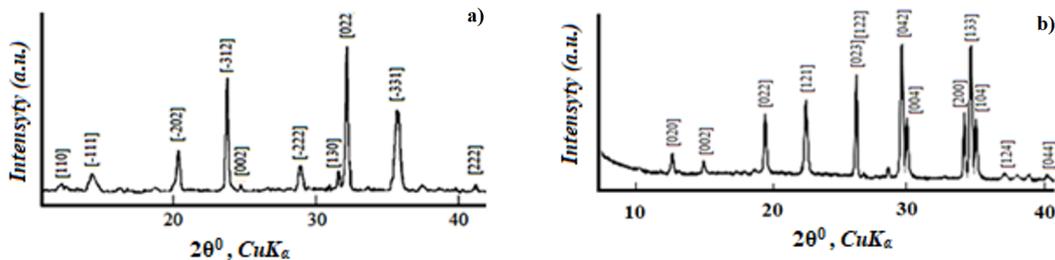


Figure 1. X-ray diffractograms of samples at room temperature: (a)  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and (b)  $\text{Na}_2\text{FePO}_4\text{F}$ .

It was also found that  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals at room temperature have orthorhombic syngony (e.g. gr.  $Pbcn$ ), and the unit cell parameters are given in Table 1. The structural parameters of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  presented in Table 1 are quite consistent with the structural data of other authors.

*Research results of the conductive properties of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$ .*

Results of measuring the temperature dependence of the ionic conductivity ( $\sigma(T)$ ) of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystal crystallites allows you to see three linear sections on the dependence  $\sigma(T)$ , corresponding to three polymorphic modifications:  $\alpha$ ,  $\beta$ ,  $\gamma$  (which are highlighted in Figure 2 with dashed lines).

The low-temperature phase of  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  can be considered dielectric, since low values of conductivity and high values of activation energy are established. At  $T_{\alpha \rightarrow \beta} = 373\text{K}$  in  $\beta$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , there is an increase in the conductivity and a decrease in the activation energy (see Table 2), which can be associated with structural changes in the crystal framework [8, 9]. Apparently, phase transition  $T_{\alpha \rightarrow \beta}$  contributes to a noticeable removal of the monoclinic distortion of the crystal framework, leading both to an increase in the concentration of mobile sodium ions and to a more uniform distribution of them in the A and B voids of the crystal framework.

Table 1.  
Structural data for  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$ .

Compositions	Temperatures $T$ , K	Space group	Unit cell parameters						
			a, A	b, A	c, A	$\alpha^0$	$\beta^0$	$\gamma^0$	V/Z
$\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$	295	C2/m	15.125	8.726	21.571	90.2	-	237.1	240.0
$\text{Na}_2\text{FePO}_4\text{F}$	295	Pbcn	5.2273	13.821	11.749	90	90	90	848.8

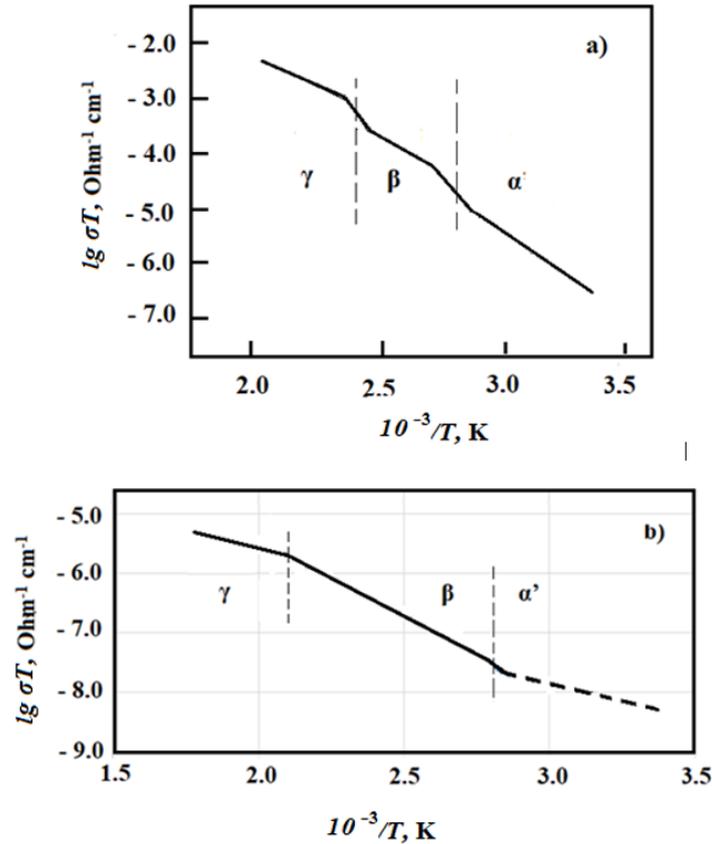


Figure 2. Temperature dependencies of the ionic conductivity  $\sigma(T)$  of grains for the (a)  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and (b)  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystalline sample (the dash-dotted line shows the  $\sigma(T)$  dependence for  $\alpha'$  -  $\text{Na}_2\text{FePO}_4\text{F}$ ).

Despite the fact that the activation energy is high for  $\beta$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , there is still a noticeable increase in the conductivity and a decrease in the activation energy at the  $\alpha \rightarrow \beta$  phase transition (Table 2) allows us to consider this phase as ion-conducting.

With a further phase transformation of  $\beta \rightarrow \gamma$ , an even greater increase in the conductivity of the polycrystal is observed, as well as a noticeable decrease in the activation energy (Table 2). These changes may be related to the complete removal of monoclinic distortions of the crystal framework in  $\gamma$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ . Therefore, the conductivity in  $\gamma$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  can be considered as superionic.

It was not possible to measure the temperature dependence  $\sigma(T)$  for the  $\alpha$  phase of  $\text{Na}_2\text{FePO}_4\text{F}$ , because according to [17], the phase transition  $\alpha \rightarrow \beta$  in this compound is possible only at a temperature of 3.4 K (due to experimental difficulties). Moreover, the  $\sigma(T)$  dependences of the sample in the temperature range from 295 to 375 K were not established, due to the instability data of the impedance meter (Figure 3 shows that, in this temperature range, the sample conductivity is highlighted by a dash-dotted line). Apparently,  $\text{Na}_2\text{FePO}_4\text{F}$  in the temperature range of 295-375 K is in a state of antiferromagnetic ordering. The reason for the instability of the impedance meter can be the noise effect which created as a result of the interaction of the applied external alternating electric field of the device and the antiferromagnetic field of the sample. The ionic conductivity of the sample was measured only at 375 K and higher temperatures. In this paper, the temperature dependences of the conductivity for  $\text{Na}_2\text{FePO}_4\text{F}$

are established only in the temperature range from 375-573 K. According to the presented in Figure 3 dependence  $\sigma(T)$ , three linear sections can be distinguished for the  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystal, which can correspond to  $\alpha'$ ,  $\beta$ ,  $\gamma$  phases. Probably, the low-temperature phase  $\alpha'$ - $\text{Na}_2\text{FePO}_4\text{F}$  is characterized by low values of conductivity and activation energy, although measurements were not performed. The reason of the low values of conductivity and activation energy of  $\alpha'$ - $\text{Na}_2\text{FePO}_4\text{F}$  can be a noticeable monoclinic distortion of the anionic crystal framework and the preservation of the antiferromagnetic ordering of the cation sublattice after the  $\alpha \rightarrow \alpha'$  phase transition. The same character of the  $\sigma(T)$  dependence was found in the dipole-ordered phases of  $\alpha - \text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  with rhombohedral framework crystal structures [18, 19]. It can be assumed that the ferrimagnetic ordering established in  $\alpha$ - $\text{Na}_2\text{FePO}_4\text{F}$  [17] is associated with the monoclinic distortion of the crystal structure of this material.

After the next phase transition  $\alpha' \rightarrow \beta$ , an increase in the conductivity and activation energy was found in the polycrystalline sample  $\beta$ - $\text{Na}_2\text{FePO}_4\text{F}$ . Moreover, the dependence  $\sigma(T)$  shows that the phase transition  $\alpha' \rightarrow \beta$  is accompanied by a small jump in conductivity at the temperature  $T_{\beta \rightarrow \gamma} = 375$  K. Apparently, this change in the conducting properties of  $\gamma$ - $\text{Na}_2\text{FePO}_4\text{F}$  is associated with further disordering of the cationic part of the crystal framework, which contributes to an increase in the concentration of sodium cations. The observed fracture on the temperature dependence  $\sigma(T)$  (at  $T_{\beta \rightarrow \gamma} = 470$  K) can be caused by the phase transition  $\beta \rightarrow \gamma$ , which leads to complete symmetrization of the crystal framework and disordering of the cation sub lattice. In this case, it is possible to increase the ionic conductivity and significantly reduce the activation energy at  $\gamma$ - $\text{Na}_2\text{FePO}_4\text{F}$ . Although  $\gamma$ - $\text{Na}_2\text{FePO}_4\text{F}$  has a low conductivity value (Table 2), the behavior on the dependence of  $\sigma(T)$  on this material is similar to the behavior of  $\gamma$ - $\text{Na}_2\text{FePO}_4\text{F}$  due to a sharp decrease in the activation energy and an increase in ionic conductivity. However, according to [14, 15], the  $\text{Na}_2\text{FePO}_4\text{F}$  structure is layered and has two-dimensional conduction channels. It is likely that the participation of fluorine in the creation of the anionic crystal framework prevents the formation of open three-dimensional conduction channels, which may be the reason for the low conductivity values in  $\gamma$ - $\text{Na}_2\text{FePO}_4\text{F}$ .

Apparently,  $\text{Na}_2\text{FePO}_4\text{F}$  has four polymorphic phase states  $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\gamma$ . By studying the dependence  $\sigma(T)$  for  $\text{Na}_2\text{FePO}_4\text{F}$ , we have established the  $\alpha'$ ,  $\beta$ ,  $\gamma$  phases and the temperature of the phase transitions  $T_{\alpha' \rightarrow \beta}$ ,  $T_{\beta \rightarrow \gamma}$  (Table 2). Note that  $\text{Na}_2\text{FePO}_4\text{F}$  the closest isostructural analog of  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  has four phases ( $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\gamma$ ) [18]. Despite significant differences in the conductivity values between  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$ , however, a general trend in the behavior of the temperature dependence of the  $\sigma(T)$  of the samples was established. Contrary to the established differences between the structure and composition of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  have common elements in the crystal structure of the rhombohedral framework crystal structures of the materials under study, which may be the cause of the manifestation of common or similar conductive properties.

The temperature dependence of the conductivity shown in Figure 2 can be described by the Arrhenius equation and, taking into account the existence of

Table 2.  
Parameters characterizing the conducting properties, as well as the phase transition temperatures for polycrystals  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$ .

Compositions / Parameters	$\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$			$\beta - \text{Na}_2\text{FePO}_4\text{F}$		
	$\alpha$	$\beta$	$\gamma$	$\alpha'$	$\beta$	$\gamma$
Conductivity, $\sigma$ , $(\text{Ohm cm})^{-1}$	$3 \cdot 10^{-8}$ $T=295 \text{ K}$	$2.6 \cdot 10^{-4}$ $T=370 \text{ K}$	$3.9 \cdot 10^{-3}$ $T=570 \text{ K}$		$6.4 \cdot 10^{-8}$ $T=400 \text{ K}$	$2.7 \cdot 10^{-6}$ $T=500 \text{ K}$
Activation energy, $\Delta E$ , eV	0.63	0.58	0.37		0,39	0.14
Phase transition temperatures $T_{\alpha \rightarrow \beta}$ , $T_{\alpha' \rightarrow \beta}$ , K	368			375		
Phase transition temperatures $T_{\beta \rightarrow \gamma}$ , K		439			470	
Dielectric permittivity values, $\varepsilon$	$10^3$ at 300 K	$1.6 \cdot 10^3$ at 400 K	$6.4 \cdot 10^4$ at 480 K	-	28 at 400 K	60 at 480 K

three phases in  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$ , its can be expressed by the relationship [18]:

$$\sigma(T) = A_i \sum_{i=1}^n \exp\left(-\frac{\Delta E_i}{kT}\right), \quad (6)$$

where  $\Delta E_i$  - the activation energy of the conductivity of the  $i$ -th phase,  $k$  is the Boltzmann constant,  $T$  is temperature, and  $A_i$  are constant coefficient that characterize the  $i$ -th phase states.

*Research results of the dielectric properties of polycrystals  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$ .*

Figure 4 shows the temperature dependences of the permittivity ( $\varepsilon(T)$ ) for  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ . It can be seen from Figure 3 that the influence of an external electric field and temperature practically do not affect the dependence  $\varepsilon(T)$ , so the low-temperature phase  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  can be considered as a dielectric one. Probably, the energy of the applied electric field to the polycrystal is not able to have a polarizing effect on the sedentary, compensated sodium dipoles in the low-temperature phase  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  (Figure 3a), since for  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  the presence of an antiferroelectric type of dipole ordering is characteristic [11].

However, with an increase of temperature of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystal, a sharp increase in the permittivity is observed in the dependence  $\varepsilon(T)$  in the region of the  $T_{\alpha \rightarrow \beta}$  phase transition =368 K (Figure 3a). The anomaly  $\varepsilon$  on the dependence  $\varepsilon(T)$  (Figure 3a), indicates a sharp increase in the concentration of polarized sodium cations resulting from the partial removal of monoclinic distortions of the crystal framework. High-temperature phases of  $\beta$ - and  $\gamma$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  are characterized by abnormally high values of the dielectric permittivity, due to the decoupling of the crystal framework. (Figure 3 does not show the values of  $\varepsilon$  for  $\gamma$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , due to the anomalously high values of this quantity).

Although it was not possible to establish the  $\varepsilon(T)$  dependence for the low-temperature phases  $\alpha$ - and  $\alpha'$ - $\text{Na}_2\text{FePO}_4\text{F}$ , these phases can be considered as dielectric, due to their antiferromagnetic ordering. When studying the  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystal on the dependence  $\varepsilon(T)$ , phase transition  $\beta \rightarrow \gamma$  was found. The low-temperature phase  $\beta$ - $\text{Na}_2\text{FePO}_4\text{F}$  is dielectric, because it is characterized by low values of  $\varepsilon$ , its weak growth on the dependence of  $\varepsilon(T)$ .

At the phase transition  $\beta \rightarrow \gamma$ , there is a sharp jump in the values of  $\varepsilon$  to the dependence of  $\varepsilon(T)$ , and with a further increase in temperature, there is a noticeable increase in the values of  $\varepsilon$  (Figure 3). This behavior of the dependence  $\varepsilon(T)$  characterizes the high polarization ability of the cationic sub lattice  $\gamma$ - $\text{Na}_2\text{FePO}_4\text{F}$  which may be associated with an increase in the concentration of mobile sodium cations in the cavities of the crystal lattice formed as a result of an increase in the symmetry of the crystal frame. Only when the cationic part of the crystal framework is completely disordered, a sharp increase in the permittivity is possible. These conclusions are consistent with the data obtained in the study of the dependence  $\sigma(T)$  for  $\text{Na}_2\text{FePO}_4\text{F}$ .

*The results of comparative analysis of the conductive properties of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals.*

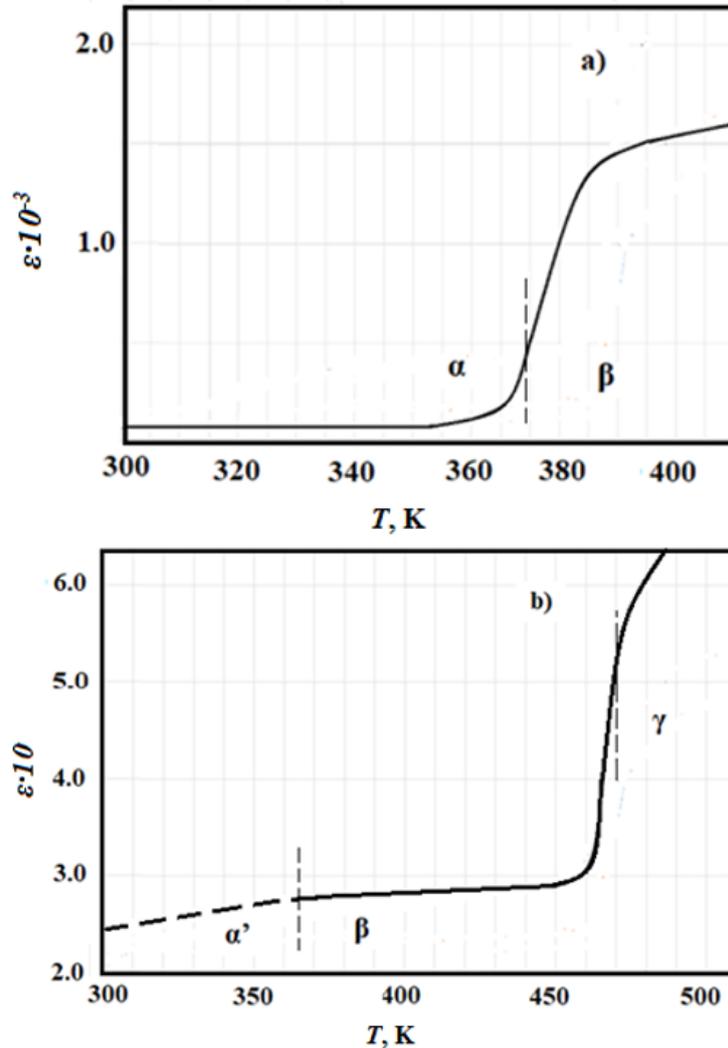


Figure 3. Temperature dependencies of the dielectric permittivity  $\varepsilon(T)$  for the (a)  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and (b)  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystalline sample (the dash-dotted line shows the  $\varepsilon(T)$  dependence for  $\alpha'$  -  $\text{Na}_2\text{FePO}_4\text{F}$ ).

By processing the obtained experimental data (see  $\sigma(T)$  and  $\varepsilon(T)$ ) we determined the phase transition temperatures, conductivity parameters, and permittivity for  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$ , which are shown in Table 2.

Table 2 shows that the ionic conductivity of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystal crystallites in various phases is one or two orders of magnitude higher than in  $\text{Na}_2\text{FePO}_4\text{F}$  samples. The observed differences in the conductivity values of the polycrystals under study may be related to the structural features of these materials. The concentration of sodium cations in  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is greater than  $\text{Na}_2\text{FePO}_4\text{F}$ . The anionic crystal rack of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  contains extensive voids of types A and B, through which sodium cations can freely move under the action of external forces [11]. Due to the openness of the crystal framework  $\{[\text{Fe}_2(\text{PO}_4)_3]^{3-}\}_{3\infty}$  and the presence of three-dimensional channels of conductivity of polycrystals  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  have good ionic conductivity (Table 2).

On the contrary, in the case of poly-anionic  $\text{Na}_2\text{FePO}_4\text{F}$  crystal frame has a layered structure with two-dimensional channels of conductivity, therefore, the conductivity of this compound may not be high.

The results of the conducting properties of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals established by us are made under the influence of an applied external electric field. According to research [20], the mechanism of electrical conductivity of the low-temperature phases of the studied samples can be hopping. Probably, the ionic conductivity in the dielectric  $\alpha$ ,  $\beta$  phases of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  can be carried out as a result of the interaction of sodium cations with the phonons of the crystal frame using an external electric field. By alternately absorbing and emitting the energy of phonons, sodium cations can periodically make the transition from the cavity to the A cavity, etc. In this case, the transfer of charge carriers is carried out due to drift under the influence of an external electric field. In this case, the value of the conductivity depends on the relaxation time and the activation energy of the charge carriers. The conductivity of the sample will be higher if the relaxation time is large and the activation energies are small. According to [19], the conductivity ( $\sigma$ ) of the sample will be equal to:

$$\sigma = \frac{n_i}{m_i} e^2 \tau, \quad (7)$$

where  $n_i$  and  $m_i$  – concentration and mass  $i$ -th of charge;  $e$  and  $\tau$  – charge and relaxation time of current carriers.

When using the same materials as cathode materials in the SIB, their conducting properties will be determined by the diffusion coefficient and the activation energy of the charge carriers. The higher ionic conductivity ( $\sigma$ ) will be in the sample where the diffusion coefficient is higher and the activation energy is lower. The conductivity of the SIB electrochemical system will largely be determined by the ability of charge carriers to diffuse processes in  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals under the action of the chemical potential of this system. From this point of view, the  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystal can provide a higher chemical potential of the SIB electrochemical system than  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ . Consequently, the  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystal is able to create conditions for faster charge and discharge processes in the SIB. Table 3 shows the diffusion coefficients ( $D$ ) and activation energies ( $\Delta E$ ) of charge carriers for  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$ .

Table 3.  
Parameters of cathode materials based on  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals.

Compositions/Parameters	$\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$	$\text{Na}_2\text{FePO}_4\text{F}$	References
Diffusion coefficients in electrodes $D$ , $\text{cm}^2/\text{s}$	$4.67 \times 10^{-12}$	$10^{-10}$	[20]
Activation energy $\Delta E$ of sodium cation migration, eV	0.45		[6]
	[100] 0.66 [001] 0.53 [010] 4.53	[20]	

The data presented in Table 3 indicate that the parameters  $D$  and  $\Delta E$  for  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  are quite acceptable to ensure normal conductivity in SIB.

The higher energy intensity values found in  $\text{Na}_2\text{FePO}_4\text{F}$ , than in  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  can be explained by the induction effect caused by a more pronounced ionic bond between iron and fluorine  $M$  cations in the chain of  $[\text{FeO}_4\text{F}_2]$  octahedra of the anionic crystal framework.

Thus, the conductive properties of polycrystals  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ ,  $\text{Na}_2\text{FePO}_4\text{F}$  depend on both the composition and structure of the crystals of these materials. It is possible to significantly increase the energy consumption of SIB when using modified polycrystals  $\text{Na}_2\text{FePO}_4\text{F}$  and  $\text{Na}_2\text{FePO}_4\text{F}$  as cathodes. Each of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals has its own advantages and disadvantages, but they can still be considered promising cathode materials for SIB, since they meet the requirements for cathode materials according to many criteria [12-15].

## Conclusion

Based on the presented experimental results, the following conclusions can be drawn:

Polycrystals  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  were obtained by solid-phase synthesis, and the structural parameters of the synthesized samples were determined.

Phase transition temperatures, conductivity and permittivity parameters for  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  are determined. It is concluded that  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  has three polymorphic phases  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\text{Na}_2\text{FePO}_4\text{F}$  has four  $\alpha$ ,  $\alpha'$ ,  $\beta$ , and  $\gamma$  phases. It is shown that the low-temperature phases  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ ,  $\alpha'$ - $\text{Na}_2\text{FePO}_4\text{F}$  and  $\beta$ - $\text{Na}_2\text{FePO}_4\text{F}$  are dielectric, and the ionic conductivity of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystals is two orders of magnitude higher than  $\text{Na}_2\text{FePO}_4\text{F}$ . It is concluded that the difference in the conductivity of these samples is related to the structural features and compositions of these polycrystals.

It is concluded that the mechanism of ionic conductivity of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals at low-temperature phases is hopping, and the parameters that determine the ionic conductivity of these materials are the relaxation time and the activation energy of the charge carriers. Parameters determining the ionic conductivity of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{FePO}_4\text{F}$  polycrystals in the SIB electrochemical system are the diffusion coefficient and the activation energy of charge carriers. The higher energy intensity values in  $\beta$ - $\text{Na}_2\text{FePO}_4\text{F}$  than in  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  can be explained by a more pronounced ionic bond between iron and fluorine cations in the chain of  $[\text{FeO}_4\text{F}_2]$  octahedra of the anionic crystal framework. It is concluded that polycrystals  $\text{Na}_2\text{FePO}_4\text{F}$  and  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  can be considered promising cathode materials for SIB.

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